

OXIDATION/Biodegradation of Solid Propellants from a 4.2-Inch Chemical Round

**Mark A. Guelta, and Mark V. Haley
U.S. Army, ECBC, APG MD 21010**

**L. Cameo Rowe
Oak Ridge Institute for Science and Education**

DoD facilities in the U.S. currently store propellants and propellant manufacturing wastes in quantities exceeding thousands of pounds. Many of these propellants were manufactured over 40 years ago with the intended purpose of configuring into chemical agent rounds or conventional high-energy mortars and projectiles. With the destruction of the US chemical agent inventory the now antiquated propellants remain in storage awaiting disposal. Re-use of these materials is unlikely due to advances in modern explosives formulations and the poor economics of converting them to other usable goods. Due to more stringent environmental regulations the traditional disposal methods of incineration and open burning or detonation are becoming more difficult to permit. Oxidation techniques have been used to treat ground water containing low-level contaminants. Studies have previously found nitrocellulose and nitroglycerine based propellants to be difficult to treat biologically. In this study oxidation using peroxide and ozone was used in combination with biodegradation to treat the neutralized solid propellants M1 and M8 that were washed out of 4.2-inch chemical rounds. The toxicity of pre and post-treatment materials was measured and compared. A combination treatment of hydrolyzed propellants with peroxone and biodegradation was effective in reducing toxicity and removing cellulose based compounds.

INTRODUCTION

The U. S. Army's Alternative Technology and Assembled Chemical Weapons Assessment¹ (ACWA) Program has effectively demonstrated the use biological treatment for destruction of chemical agents removed from chemical rounds stored at Pueblo Chemical Depot². The same biological treatment schemes used for chemical agents have not worked well for destruction of the propellants removed from these chemical rounds. While a neutralization/biodegradation solution has been approved for full-scale design at the Pueblo Chemical Depot site for destruction of agent containing munitions, an alternative method for destroying the potentially contaminated propellants has not been decided. Mixed bacterial cultures in immobilized cell bioreactors grown on hydrolyzed mustard agent were unable to degrade or detoxify the hydrolyzed propellants feeds under similar treatment conditions. Alternative biotreatment schemes were proposed but never attempted for propellants specific to the Pueblo site.

In an unrelated program the Army Environmental Center³ used advanced oxidative processes (AOP) in the treatment of explosives in contaminated groundwater from Cornhusker Army Ammunition

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Plant⁴. In these instances oxidative processes including treatment with ozone and peroxide were able to reduce explosives to less than 1 ug/L. While the oxidative approaches have worked well for elimination of the low level contaminants, pump and immobilization on filter beds for later destruction has been a preferred treatment method. This practice is based on the longer track record of pump and treat systems, the later development of AOP and the higher initial capital costs that can be associated with some AOP.

DeFrank and Guelta⁵, successfully used ozone treatment to destroy di-sulfide compounds in VX nerve agent hydrolysates up to 5 percent mixed with component B explosives from chemical rounds. The pretreatment of the hydrolyzed VX nerve agent allowed biotreatment with mixed bacterial cultures to 5% and bleached out the colored comp. B so that downstream treatment with UV/peroxide could be attempted. In a separate study UV/peroxide treatment was used to breakdown phosphonate and di-sulfide compounds that had demonstrated resistance to biotreatment.

In this study the utility of ozone combined with peroxide treatment will be examined for its ability to detoxify and breakdown mixed nitrogen and nitrocellulose compounds that were previously shown resistant to biodegradation. Two hydrolyzed propellants, M1 and M8, removed from assembled chemical rounds were treated with combined ozone and peroxide (peroxone) and treatment in immobilized cell bioreactors. Another goal of the study is to remove nitrogen compounds known to be present to levels that may allow discharge of the biotreated effluents to surface waters or a wastewater treatment system.

METHODS

In this study we examined hydrolyzed propellants M1 and M8 removed from chemical rounds. The propellants were hydrolyzed at 1% (wt/vol) loading in 6 percent NaOH solution. The mixture was hydrolyzed at 90 °C for 4 hrs before cooling and coarse filtering. These hydrolysates were treated with ozone and peroxide (peroxone) to reduce their toxicity to biological cultures. Two separate treatment schemes were used to evaluate the effectiveness of the AOP treatment. Immobilized Cell Bioreactors were used to compare biotreatability of the peroxone treated and untreated hydrolyzed propellants. Table one lists the general recipe for the M1 and M8 propellants prior to hydrolyzation.

TABLE 1 Composition of M1 and M8 propellants.

M1 Propellant Composition		M8 Propellant Composition	
Compound	% wt/wt	Compound	% wt/wt
Nitrocellulose	84	Nitrocellulose	52.15
Dinitrotoluene	9.0	Nitroglycerine	43.0
Dibutylphthalate	5.0	Diethylphthalate	3.0
Diphenylamine	1.0	Potassium nitrate	1.25
Lead carbonate	1.0	Ethyl centralite	0.60

The propellants were diluted to a concentration of 200 ml/L. This biofeed solution was fed to the bioculture directly or first treated with the peroxone. Hydrogen Peroxide (30mls of 35%) was added to each liter of solution to be treated. Ozone was generated at approximately 1.25 grams/hour. Upon completion, the oxidized solution was pH adjusted to below 9.0 with HCl and any remaining peroxide removed by the addition of catalase.

Timed peroxone and biotreatment samples were monitored for toxicity using the Microtox (MTX) assay. The MICROTOX assay exposes a bioluminescent marine bacterium (*Vibrio fischeri*) to a sample of unknown toxicity and measuring the change in light output, indicating metabolic activity. Data was analyzed with the MTX Test Protocol software to determine the EC₅₀ (the effective concentration causing a 50% reduction in light output). The Microtox assay has been proved to be a good measure of substrates toxicity to biocultures used in earlier studies^{6,7}.

Periodic samples were also analyzed for Chemical Oxygen Demand (COD), ph, phosphate, nitrate and nitrite levels. These tests were conducted using Hach spectrometer assays kits.

Two strategies were tested for oxidation and biotreatment of the hydrolyzed propellants.

Strategy 1

Hydrolyze → Biotreat(1) → Oxidize (3 hrs) → Biotreat(2)

Strategy 1 consisted of treating the propellant hydrolysate directly with mixed biocultures seeded with activated sludge in immobilized cell bioreactors (ICB) without peroxone treatment. This step uses the carbon compounds available to the bioculture to drive metabolism that can denitrify the nitrogenous media compounds under anoxic conditions. The effluents from the first biotreatment stage is filtered to remove biomass and subjected to peroxone treatment for 3-hrs. A secondary biotreatment was then used to treat the now oxidized nitrocellulose compounds left untreated by the first stage biotreatment.

Strategy 2

Hydrolyze → Oxidize (6 hrs) → Biotreat (2 stages)

Strategy 2 consisted of pretreating the same concentration of biofeed for 6-hrs in the peroxone reactor. The media would also receive a secondary biotreatment that includes addition of carbon as glucose to increase metabolism and denitrification.

The Immobilized cell bioreactors are 600 ml each glass vessels with a single port top and bottom for input/output. The top is open but fitted with butyl rubber stoppers. The stoppers are ported to allow pH monitoring and control, feed and nutrient addition and exhaust gas release to a trap. pH was controlled in one direction only with 0.5N HCl. Stage 1 of the reactors was operated at a 5-day hydraulic residence time (Hrt). Stage two of the reactors were operated at a 10-day Hrt. Stage 1 was intended to degrade the hydrolyzed feed as best possible and remove excess nitrogen in the form of nitrite and nitrate through denitrification. Reactors were inoculated with sludge from a public wastewater treatment plant, then acclimated and grown on their respective feedstock. The reactors were operated anoxically to encourage

denitrification. In the second stage an additional carbon feed source was added to increase metabolic activity and denitrification. Within each feed type (M8 or M1) reactors were labeled as series one or two.

RESULTS

Strategy 1

In strategy 1 the biofeeds are prepared at 200 ml/L of the propellant hydrolysate. The biofeed was administered to the culture over a 30 min. period, once per day. Representative samples of the feed and effluents were taken after initial acclimation and biomass ramp-up period when the reactors were considered to be at steady state. These samples were assayed for Chemical Oxygen Demand (COD), nitrite, nitrate and phosphate concentrations. The levels of nitrogen compounds are significant in that they are principal breakdown products of the propellants nitrocellulose base, Dinitrotoluene, Nitroglycerine, and mixed nitrogen compounds. These compounds before neutralization are fairly toxic to aquatic species. When not completely removed during biotreatment they are closely regulated pollutants, or nutrients when considered for release to surface waters or waste water treatment systems. Figure 1 below represents results of these assays for COD, nitrate and nitrite during strategy 1 biofeed stage 1 and the 3-hour peroxide/ozone (peroxone) treatment of M1 propellant. The stage-1 biotreatment greatly decreased media COD and nitrite concentrations. In an anoxic culture nitrite oxygen is used as an electron donor during metabolism of available carbon in place of dissolved oxygen. Therefore metabolism of the available carbon (COD) results in removal of nitrite (denitrification) and liberation of nitrogen gas.

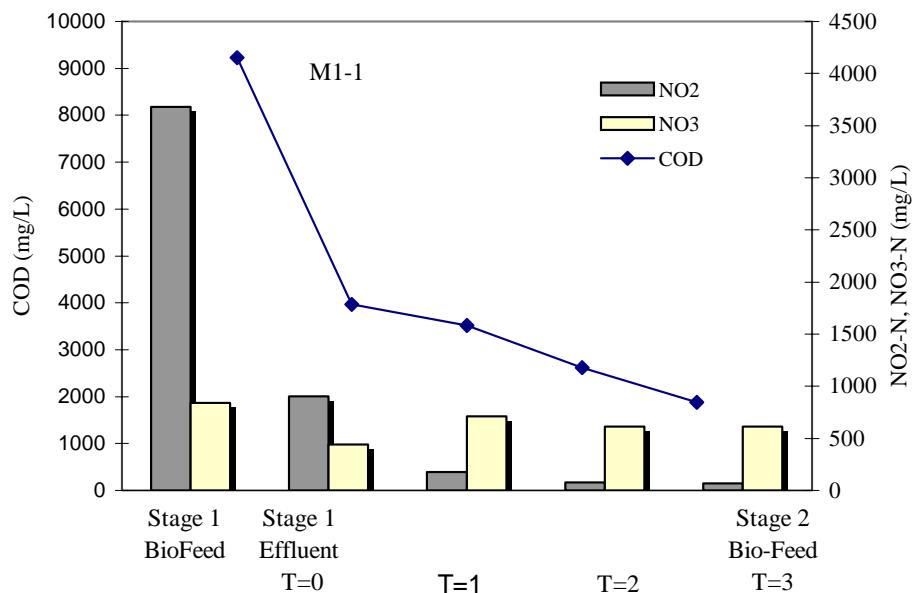


Figure 1 Results of chemical oxygen demand, nitrate and nitrite assays of M1 feeds and 3-hour peroxone treatment.

The peroxone treatment removes additional COD and more recalcitrant carbon remaining after stage 1 biotreatment. Available nitrite is oxidized to nitrate. The nitrate must be removed during the stage-2 biotreatment process to yield nitrogen levels below regulatory discharge requirements. Discharge requirements differ by state consult specific state permitting regulations.

Figure 2 displays results of COD and nitrogen assays for M8 propellants during strategy 1. COD removal during initial biotreatment seems greater in the M8 biotreatment than in M1. From figure 3, the greater detoxification of M8 media is also apparent following biotreatment 1.

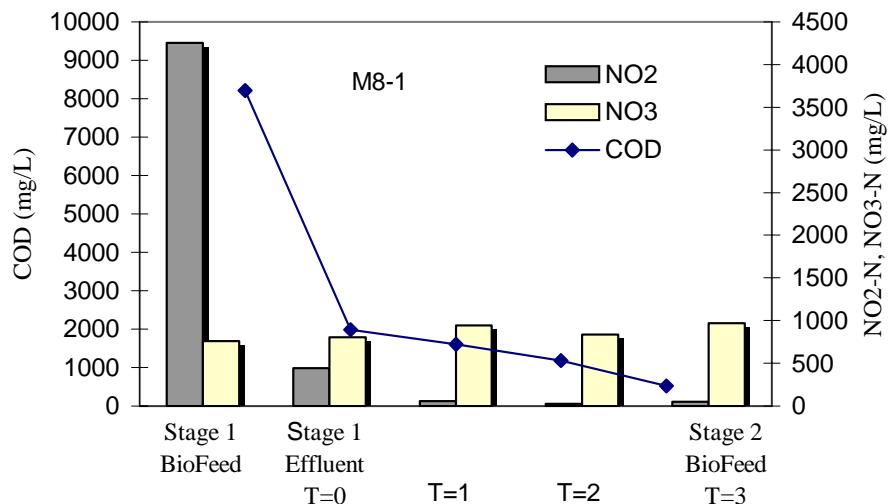


Figure 2 Results of chemical oxygen demand, nitrate and nitrite assays of M8 feeds and 3-hour peroxone treatment.

Despite the initial higher toxicity of M8 biofeed, the M8 appears to be more treatable with stage-1 biotreatment than the M1. Treatment of stage 1 biotreatment effluents with peroxone further detoxifies and removes more recalcitrant COD from the media but has little effect on total nitrogen. Further treatment is required to remove excess nitrogen, a closely regulated nutrient in surface and wastewaters.

An increase in the Microtox values indicates a decrease in the toxicity of the propellant feed to the *Vibrio fischeri*. This data can be used, as an indicator as to how well the bacterial in the ICB will respond to the biofeed. While it may not be an indication of success of the treatment, it does indicate the level of toxicity the biofeed may have on the bioreactor culture and the environment if released. In Figure 3 below are the Microtox results for the “Strategy 1” approach of stage-1 biodegradation followed by 3-hours of peroxone treatment and a second, stage-2, biotreatment for the M1-1 and M8-1 bioreactor series.

Microtox results from strategy 1 indicate that the M8 biofeed is initially more toxic than the M1. Each is detoxified to different degrees by the stage 1 biotreatment. Each propellant is further detoxified by the 3-hr peroxone treatment and completely detoxified, according to Microtox, by completion of stage-2 biotreatment. EC50’s for final effluent are greater than the 100 % reported here indicating the effluent is not only non-toxic but has become nutritive to *Vibrio fischeri*.

The overall effectiveness of the strategy 1 approach for both propellant types studied is presented in figure 4 below. For each material, COD and nitrogen content is decreased approximately 50% by the initial, stage-1, biotreatment. COD is further decreased by the peroxone treatment. Total nitrogen levels remain constant over the course of the 3-hr peroxone treatment. During the stage-2 biotreatment total nitrogen levels are decreased to near regulatory limits. Final effluent COD level does not decrease in the final M8 effluent, however approximately 3000 mg/day exogenous carbon is added and consumed. The M1 final effluent COD does decrease over the stage-2 feed level even with the addition of the 3000 mg/day glucose.

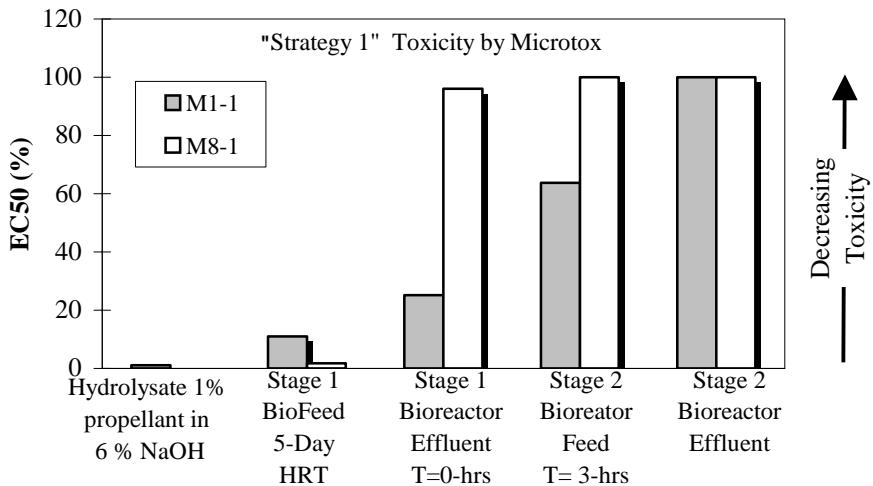


Figure 3 Results of Microtox analysis of strategy 1 biofeeds and effluents.

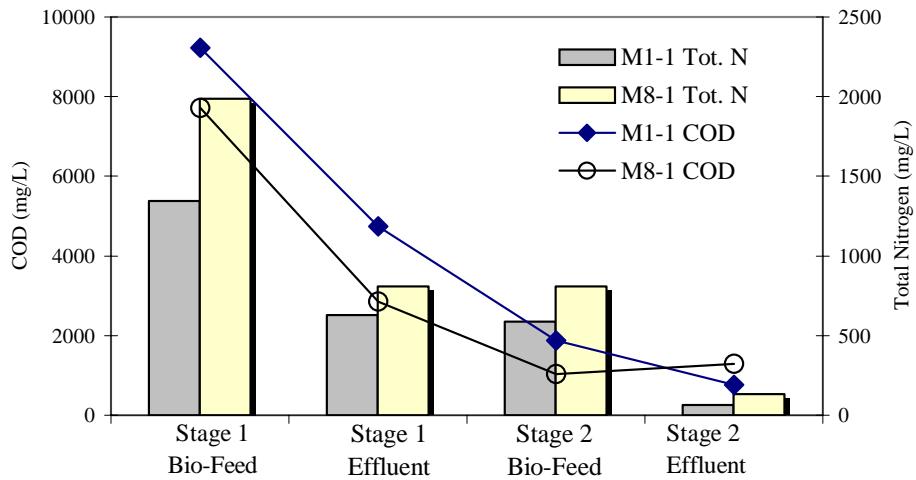


Figure 4 Results of overall COD and total nitrogen analyses for M1 and M8 propellants.

Strategy 2

During the oxidation process easily oxidizable COD is removed and media nitrite is converted to nitrate. This is similar to conversions in the strategy 1 peroxone treatment except that in strategy 2, the COD that is easily broken down during biotreatment is probably removed before more recalcitrant compounds. For the samples analyzed, starting nitrogen levels are also higher than with strategy 1.

During the 6-hour peroxone treatment COD is quickly removed and the initially higher levels of nitrite are converted to nitrate. The increased nitrate levels required additional denitrification to get below allowable discharge limits. The addition of an exogenous carbon source in the secondary biotreatment stage boosts metabolism and oxygen requirements thus increasing the rate of denitrification. However, the nitrate-nitrogen represents a greater denitrification challenge than nitrite ion. In figures 5 and 6 the removal of COD and conversion of nitrite to nitrate during the 6-hour peroxone treatment is easily

recognizable. The COD removal and oxidation of nitrite to nitrate occurs more quickly during M8 peroxone treatment than it does in M1 media.

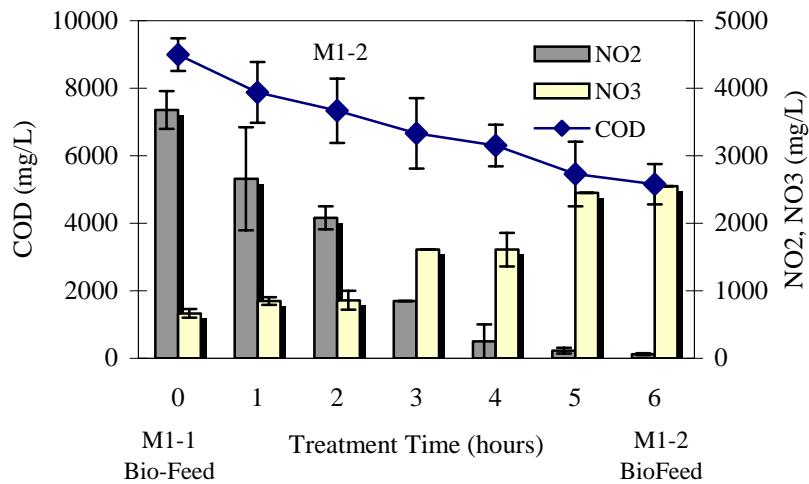


Figure 5 Results for COD, nitrate and nitrite values for 6-hour peroxone treatment of M1 Propellant.

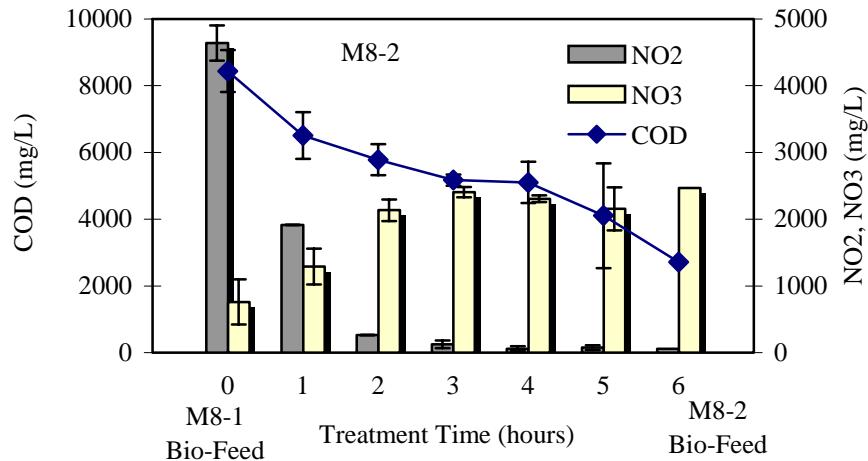


Figure 6 Results for COD, nitrate and nitrite values for 6-hour peroxone treatment of M8 Propellant.

Figure 7 shows results for microtox data during the strategy 2 treatments. This method also produces a final effluent that is non-toxic, according to microtox, and may act as a nutrient to aquatic microorganisms. Again M8 initially appears more toxic than M1 but is more quickly oxidized and detoxified than M1.

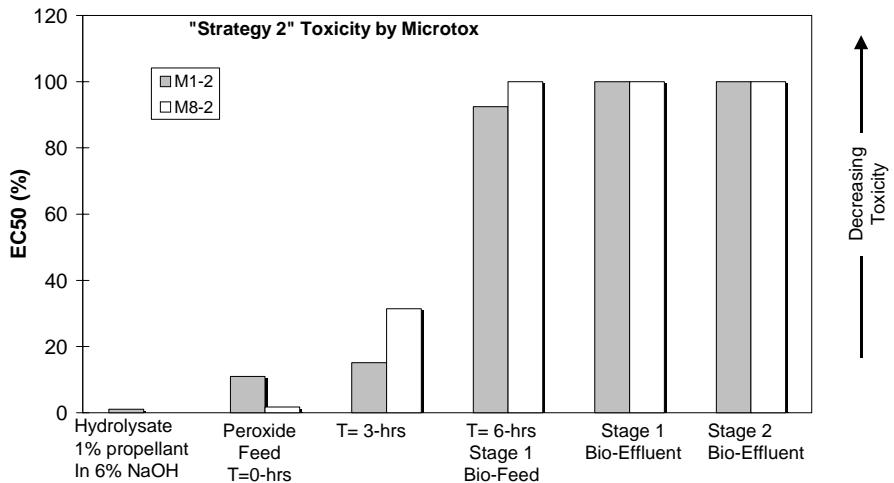


Figure 7 Results of Microtox analysis of “Strategy 2” feeds and effluents

Overall strategy 2 results are presented in figure 8 below. The initial COD displayed represented a decreased value from peroxone treatment over the initial COD levels for the untreated strategy 1 stage-1 feed. M8 appears initially to have greater total nitrogen levels, but are treated to very low levels by the end of the stage 2 biotreatment. M1 COD and total nitrogen appear more difficult to remove with COD and nitrogen levels slightly higher through the stage 2 biofeed. M8 COD appears more easily removed during peroxone treatment and stage-1 biotreatment. Final COD levels are elevated due to several carbons over feedings during the study. Media carbon did reach below 500 mg/L on several occasions but the overall COD for the final composite sample is artificially high.

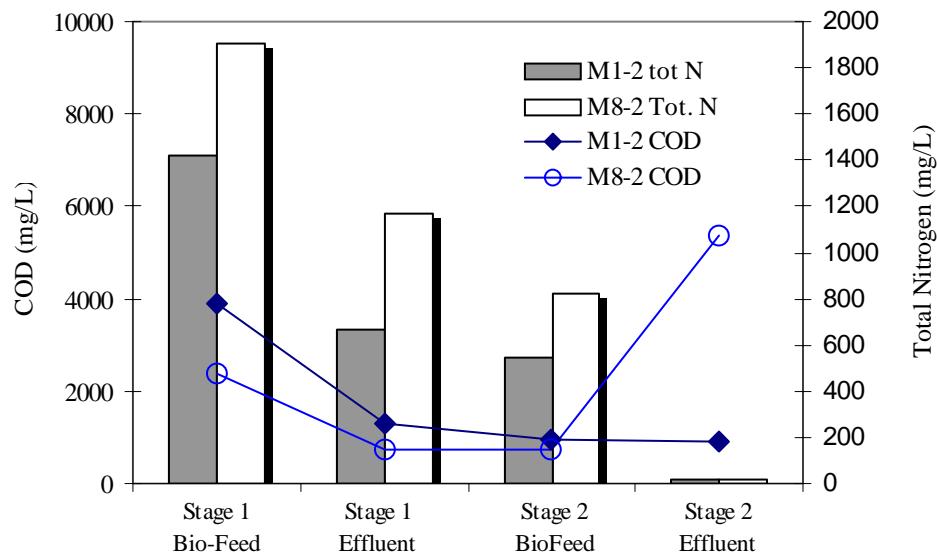


Figure 8 Results of overall COD and total nitrogen analyses for M1 and M8 propellants.

CONCLUSION

Success of the combined oxidation/biotreatment on detoxification and removal of nitrogen from the effluents was reasonably high. Figures 4 and 8 show the results of each step of the two treatment strategies. The peroxone treatment of the biofeed resulted in removal of easily oxidizable carbon. More recalcitrant compounds became more bio-available as demonstrated by the cultures ability to remove COD beyond the stage 1 effluent concentration.

The 6-hour pretreatment of bio-feed for strategy 2 followed by biotreatment seemed to be the most successful off the two strategies, although both strategies worked well. The lower values for total nitrogen are within benchmarks for release to many states public wastewater treatment systems. System effluent phosphate that was added for nutritional support, but not reported here, were consistently below regulatory limits and should not be an issue for permitting purposes.

Strategy 1 utilized the bio-available carbon to remove over half the total propellant nitrogen prior to the 3-hour peroxone treatment. Although the strategy 1 treatment system did not work as well during this study it merits further investigation. Much of the success of a biotreatment approach depends on selection and control of appropriate culture stock. There were several pH and feeding upsets during this study that while proving the robustness of the approach, may have caused some acclimation and developmental setbacks. The concept post treatment of stage 1 effluent using the strategy 1 approach should save energy and processing costs provided the biomass could be separated economically from the effluent. Certainly a tangential flow or reversible flow membrane system would fill this function.

In table 2 below are the reported total nitrogen feed and effluent levels within the system. Also listed are calculated levels for nitrogen input and output based on daily input per liter of total reactor volume. For this scenario the second stage biotreatment is twice that of the first. During the study stage-1 operated at a 5-day hrt, stage-2 operated at 10-day hrt, even though reactor volumes were the same.

TABLE 2 Total nitrogen system throughputs.

	Total Nitrogen Concentration			Total Nitrogen Input/Output	
	Starting Bio-Feed (mg/L)	Stage-2 Biofeed (mg/L)	System Effluent (mg/L)	Input (mg/Day/L)	Output (mg/Day/L)
M1-1	1622	588	66	83.1	33.8
M8-1	2095	808	134	107.4	6.9
M1-2	1622	542	17.4	83.1	8.9
M8-2	2095	825	14.7	104.4	0.75

Effluent carbon could easily be managed to a lower discharge concentration. A single multi-head tubing pump that did not deliver dependable daily dosages of exogenously added carbon. Pump operation was repeatedly problematic. The elevated COD reported for M8-2 should not be a deterrent for any proposed system. The use of glucose as an added carbon could easily be substituted with a low cost, locally available carbon rich waste stream from a food processing plant.

Each of the treatment schemes also effectively detoxified the propellant hydrolysates. Final effluent was non-toxic and became nutritive to the luminescent bacteria and encouraged elevated activity during Microtox assay. Partially treated effluents would be a nutrient source if released to surface waters and therefore would be closely regulated.

The utility of a low cost, low-tech advanced oxidation/biotreatment scheme has been proven in this laboratory scale system. A system of this nature should be considered for the treatment of propellant wastes or antiquated stock should more traditional open burn/open detonate methods become restrictive. The two compounds used in this study did not react uniformly to similar oxidation treatment. The exact design and operation can be advanced and may be material specific. Additional study is recommended at the pilot scale. As of this writing additional work is underway using other antiquated, heavily stocked materials.

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